Hyperfine frequency shift in two-dimensional atomic hydrogen

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We propose the explanation of a surprisingly small hyperfine frequency shift in the two-dimensional (2D) atomic hydrogen bound to the surface of superfluid helium below 0.1 K. Owing to the symmetry considerations, the microwave-induced triplet-singlet transitions of atomic pairs in the fully spin-polarized sample are forbidden. The apparent nonzero shift is associated with the density-dependent wall shift of the hyperfine constant and the pressure shift due to the presence of H atoms in the hyperfine state a not involved in the observed $b \to c$ transition. The interaction of adsorbed atoms with one another effectively decreases the binding energy and, consequently, the wall shift by the amount proportional to their density. The pressure shift of the $b \to c$ resonance comes from the fact that the impurity a-state atoms interact differently with the initial b-state and final c-state atoms and is also linear in density. The net effect of the two contributions, both specific for 2D hydrogen, is comparable with the experimental observation. To our knowledge, this is the first mentioning of the density-dependent wall shift. We also show that the difference between the triplet and singlet scattering lengths of H atoms, $a_t - a_s = 30(5)$ pm, is exactly twice smaller than the value reported by Ahokas *et al.*, Phys. Rev. Lett. **101**, 263003 (2008).

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Hyperfine atomic transitions, which are currently used as frequency standards [1] for their extreme stability, experience a frequency shift due to the interaction of resonant atoms with the container walls, buffer gas and with each other. These are commonly referred to as the wall shift, pressure shift and contact shift, respectively. The contact or collision shift is associated with a difference in the scattering length of atoms in two hyperfine states coupled by the resonance. It has been shown quite convincingly, both in theory and experiments with ultracold alkali vapors, namely, with bosonic ^{87}Rb [2] and fermionic ^{6}Li [3], that the measured resonance shift due to the interstate collisions is independent of the coherence and polarization in the two-level system and fully determined by the statistics of atoms: the magnitude of the shift is the equilibrium energy splitting between the two internal states in a fully decohered cloud multiplied by the two-particle correlation function, which is $g^{(2)} = 1$ for distinguishable particles and Bose-Einstein condensates, $g^{(2)} = 2$ for thermal bosons and $g^{(2)} = 0$ for fermions [3].

It is especially surprising in this context that the hyperfine frequency shift recently observed in the 2D Bose gas of spin-polarized atomic hydrogen (H↓) appeared to be a factor of ~ 120 less than expected [4]. This contradiction, i.e., the virtual absence of the contact shift and the respective "fermionic" behavior of atomic hydrogen, has been lately resolved by taking into account a symmetry selection rule that forbids the electronic triplet-singlet transitions of atomic pairs: under the absorption of microwave quanta, the electron spins of all atoms experience coherent rotation being parallel to each other so that the interaction energy does not change [5]. However, the nature of the small yet nonzero hyperfine frequency shift in atomic hydrogen remained unclear. The question was lately addressed by Hazzard and Mueller [6] and Ahokas *et al.* [7]. However, as we show below, their arguments are contradictory at some points and incomplete.

In this Letter, we propose the alternative explanation of the apparent frequency shift in 2D atomic hydrogen based on the independent action of two different factors, the density-dependent wall shift and the pressure shift due to the residual atoms in the hyperfine state that is not involved in the observed resonance and has the opposite projection of a nuclear spin. We also show that the difference between the triplet and singlet scattering lengths of H atoms, $a_t - a_s = 30(5)$ pm, is exactly twice smaller than the value reported in Ref. [7].

The ground state of a H atom in a magnetic field B is split into four hyperfine states (in the $|m_s, m_i\rangle$ basis in the order of increasing energy):

$$a = \cos\theta|-+\rangle - \sin\theta|+-\rangle, \;\; b = |--\rangle,$$
$$c = \cos\theta|+-\rangle + \sin\theta|-+\rangle, \;\; d = |++\rangle,$$

where $\pm$ stands for $\pm\frac{1}{2}$, $\tan(2\theta) = A[(\gamma_e + \gamma_p)hB]^{-1}$, $\gamma_e(\gamma_p)$ is the electron (proton) gyromagnetic ratio and $A/h = 1420$ MHz is the hyperfine constant of hydrogen. The experiments [4] with 2D hydrogen were carried out at $T \sim 0.1$ K in the high field $B = 4.6$ T such that $\gamma_e hB \gg A, k_BT$ and therefore the electron spins of atoms are polarized. Moreover, the sample is almost entirely in the doubly-polarized state b. The resonance line of the electron spin-flip $b \to c$ Zeeman transition of the atoms adsorbed on a liquid helium surface is shifted with respect to the resonance of the gas-phase atoms by the dipole field B_d imposed by spin-aligned atoms on each other [8]. To exclude the unwanted dipole contribution, Ahokas *et al.* used another, nuclear spin-flip, $b \to a$ transition as a reference. The latter was supposed to be free

from the contact shift.

In the high-field ($\gamma_e \hbar B \gg A$) approximation, the frequency difference of the $b \to a$ resonance on the surface and in the bulk gas is [4]

$$\Delta\nu_{ab} \equiv \nu_{ab}^s - \nu_{ab}^0 = \frac{\Delta A_w}{2h}\left(1 + \frac{\gamma_p}{\gamma_e}\right) - \frac{\gamma_p}{\gamma_e}\Delta\nu_c. \qquad (1)$$

Here ΔA_w is a change in the hyperfine constant due to the interaction with liquid helium and $\Delta\nu_c$ is the expected contact shift of the $b \to c$ resonance. In fact, ΔA_w also known as the wall shift is proportional to a change in the unpaired electron density at the proton due to the distortion of the electron wavefunction of the atom in the adsorption potential. $\gamma_p/\gamma_e \approx 1.5 \times 10^{-3}$ may be safely neglected with respect to unity. Note, that the $b \to a$ transitions on the surface and in the bulk gas are excited in different external fields, such that the frequency of the respective $b \to c$ resonance does not change.

Experimentally, $\Delta\nu_{ab}$ is linear in the surface density σ_b of atoms in the hyperfine state b

$$\Delta\nu_{ab} = C_0 + C_1\sigma \qquad (2)$$

with $C_0 = -24.79(2)$ kHz and $C_1 = 1.52(15) \times 10^{-9}$ Hz·cm^2 [4]. Ahokas *et al.* attributed this entirely to the density variation of the contact shift $\Delta\nu_c$. Thus, the values actually quoted in Ref. [4] were those derived for ΔA_w and $\Delta\nu_c$. They further argued that, like in alkalies, $\Delta\nu_c$ should be proportional to a difference $a_t - a_s$ between the triplet $b-b$ and singlet $b-c$ scattering length in the initial and final state, respectively. Owing to a small value of C_1 ($\sim$ 120 times less than expected), Ahokas *et al.* concluded that the scattering lengths are probably considerably different from the common values, $a_t = 0.72$ and $a_s = 0.17$ Å [9].

Shortly after that, Safonov *et al.* [5] showed that, due to the symmetry constraints, both electronic and nuclear triplet-singlet transitions of atomic pairs are strictly forbidden in the spatially uniform sample hundred-percent polarized in both electron and nuclear spins. In fact, scattering of two atoms is determined by their total spin F, whose parity gives the parity of the relative angular momentum, i.e., the possibility of the s-wave scattering, and the total electron spin S, which determines the interaction potential (singlet or triplet) and therefore the scattering length. The initial spin wavefunction of two b-state atoms ($F = 2$, $m_F = -2$; $S = I = 1$, $m_S = m_I = -1$) is *symmetric* with respect to the permutation of particles. The same holds for their unperturbed Hamiltonian and the perturbation Hamiltonian due to the microwave field. Consequently, the final state after the absorption of a microwave photon $|bc\rangle_g = \frac{1}{\sqrt{2}}(|bc\rangle + |cb\rangle)$ is also *symmetric*. Thus, the total spin F must remain even. The total electron and nuclear spins are necessarily conserved: $S = I = 1$. Notably, this holds in an arbitrary magnetic field, which is easily verified by evaluating $\langle bc|\hat{S}^2|bc\rangle_g$ and $\langle bc|\hat{I}^2|bc\rangle_g$. In a classical interpretation, all electron spins of the ensemble of hydrogen atoms are coherently tilted so that each atomic pair constitutes an electronic triplet, just like in the initial state. Thus, the contact shift $\Delta\nu_c$ must be exactly zero irrespective of the actual values of the scattering lengths a_t and a_s. The revision of a_t and a_s is therefore unnecessary. The situation with the nuclear $b \to a$ Zeeman transition is obviously identical.

Recently, Hazzard and Mueller [6] tried to explain the smallness of the hyperfine shift in the 2D hydrogen in a different way. They suggested that the substrate-mediated H-H interaction is substantially different from the interaction of free atoms and concluded that the hyperfine frequency shift of the $b \to c$ transition must be much *lower* in the adsorbed phase, as compared to the bulk gas. However, they quite arbitrarily ignored the above symmetry arguments, which imply that the contact shift of the $b \to c$ and $b \to a$ transitions is exactly zero in both 2D and 3D cases, as long as the gas is doubly spin-polarized. This makes the theory of Hazzard and Mueller irrelevant in this respect. Note, that Ahokas *et al.* [7], who basically repeated the arguments of Ref. [5] regarding their measurements of the contact shift in the 3D atomic hydrogen, also came to a conclusion that the shift of the $b \to c$ transition is zero in the doubly polarized gas. In addition, the conclusion of Ref. [6] contradicts with the observation [4, 7] that the contact shift in the 2D gas is *higher* than in the bulk phase, as follows from comparison of the respective experiments.

Safonov *et al.* [5] discussed the opportunity that the frequency shift of the $b \to c$ transition may be nonzero due to the dipole-dipole interaction of electron spins. It was asserted that the dipole-dipole interaction is symmetric with respect to the permutation of atoms and therefore does not break the symmetry constraint for the hyperfine transitions of atomic pairs. However, Ahokas *et al.* [7] attributed the nonzero shift to the dipole mechanism saying that the dipole-dipole interaction is long-range and must be treated separately. Unfortunately, in their brief discussion, they did not show how the symmetry constraint is lifted by the dipole-dipole interaction. Neither they explained the difference between this mechanism and the usual dipole shift of the hyperfine resonance due to the internal magnetic field B_d imposed by spin-polarized atoms on each other. In this regard, it is crucial to show that this effect acts differently on the $b \to c$ and $b \to a$ transitions, otherwise it cannot be detected by the technique of Ref. [7]. It is also unclear how all this applies to the 2D case. Ref. [7] refers to the future publication of the calculation details, which does not allow a more specific discussion of the subject.

However, there is another reason for $\Delta\nu_c$ to be nonzero in hydrogen. This is due to the residual atoms in the hyperfine state a that are always present in the sample owing to spontaneous one- and two-body nuclear relaxation followed by relatively fast recombination with b atoms

into H_2 molecules. The role of these third-state atoms in the 3D case has been demonstrated in recent experiments of Ahokas *et al.* [7]. However, their results for the magnitude of the contact shift $\Delta\omega_{ad}$ of the $a \to d$ transition in the b-state gas and the interaction energy E_{ab} of a and b-state atoms are exactly one-half of the respective values obtained in Ref. [5]. We believe that this difference in $\Delta\omega_{ad}$ and E_{ab} originates from the fact that, in the calculation of the interaction energy, the authors of Ref. [7] considered hydrogen atoms in different hyperfine states as *distinguishable* and used $g^{(2)} = 1$. At the same time, they expressed the diatomic states in terms of electronic and nuclear singlets and triplets, which assumes *identical* particles with $g^{(2)} = 2$ and includes their "distinguishability" automatically, via the ratio of symmetric and antisymmetric contributions to the diatomic wavefunction. As a result, the difference in the scattering length quoted in Ref. [7] must be divided by 2, which yields $a_t - a_s = 30(5)$ pm. This is somewhat lower than the theoretical values [9].

The fraction of a atoms is typically very small and difficult to detect by ESR. Therefore, we neglect the interaction of these atoms with each other. The interaction energies of ac and bd pairs are essentially the same [5]. Thus, the shift of the $b \to c$ resonance in the presence of a atoms is (cp. Eq. (2) of Ref. [7] with the above-said factror-of-two correction and Eq. (8) of Ref. [5])

$$\Delta E_{\text{int}} \equiv h\Delta\nu_{bc} = \frac{2\pi\hbar^2}{ml}(a_s - a_t)\sigma_a, \tag{3}$$

where σ_a is the 2D density of a atoms and $l \sim 5$Å is the delocalization length of adsorbed atoms' wavefunction in the surface-normal direction.

Let us now consider the rate equations including relaxation and recombination to evaluate the steady-state density of a atoms. In the experiments under consideration, the great majority of hydrogen atoms, predominantly in the b state, is in the gas phase in the sample cell volume. On the other hand, nearly all recombination and relaxation events occur in the 2D phase adsorbed on either the low-density "warm" ($T_0 = 120 - 200$ mK) cell walls or on the high-density cold spot ($T_s = 50 - 90$ mK) [4, 10]. Thus, the total number of a atoms in the cell obeys the rate equation

$$\begin{aligned}\dot{N}_a = \Phi_a + A(G_1\sigma_b + G_2\sigma_b^2 - K_{ab}\sigma_a\sigma_b) + \\ +A_s(G_{1s}\sigma_{bs} + G_{2s}\sigma_{bs}^2 - K_{abs}\sigma_{as}\sigma_{bs}).\end{aligned} \tag{4}$$

Here Φ_a is the flux of atoms from the low-temperature dissociator/polarizer [4] and G_1, G_2 and K_{abs} are the rate constants of, respectively, one- and two-body nuclear relaxation and exchange recombination on the cell walls. The subscript s refers to the values on the cold spot. The area of the cell walls and the cold spot is $A \sim 100$ cm^2 and $A_s = 0.32$ cm^2, respectively. The ratio of the equilibrium b-atom density on the cold spot to that on the cell walls is $\sigma_{bs}/\sigma_b \approx \exp[E_a(T_s^{-1} - T_0^{-1})]$, which amounts to about $3{\times}10^4$ at $T_0 = 200$ mK and $T_s = 70$ mK. Therefore, $\alpha \equiv A\sigma_b/A_s\sigma_{bs} \sim 0.1$. In this case, the two-body relaxation on the cell walls may be safely omitted. In addition, it is reasonable to assume that $\sigma_a \ll \sigma_{as}$. Then, in the steady state ($\dot{N}_a = 0$), neglecting the incoming flux Φ_a we obtain

$$\sigma_{as} \approx \frac{G_{1s} + \alpha G_1}{K_{abs}} + \frac{G_{2s}}{K_{abs}}\sigma_{bs}. \tag{5}$$

Thus, the density of a atoms on the cold spot is linear in the density of b atoms. In experiment, $\dot{N}_b = 0$ is maintained. This implies that the flux of b atoms replenishes the recombination losses of atoms in both hyperfine states (they recombine in equal numbers). Obviously, due to the operation of the polarizer, $\Phi_a \ll \Phi_b$. Therefore, the smallness of Φ_a in Eq. (4) is verified.

The rate constant of the first-order nuclear relaxation on the cell walls is $G_1 \sim 0.1$ s^{-1} [4]. G_{1s} is probably close to G_1. According to Safonov *et al.* [11], $K_{ab} = 2.8\times10^{-9}\cdot T^{3/2}$ cm^{2}K$^{-3/2}$s^{-1} $\simeq 5\times10^{-11}$ cm^{2}s^{-1} at 70 mK. In theory, the two-body relaxation rate constant is zero if the surface is exactly normal to the ambient field [12]. However, this was never observed in experiment. The experimental estimate for the field of interest obtained from the multi-parameter fits of the decay curves is $G_{2s} \lesssim 4\times10^{-13}$ cm^2/s [13]. The theoretical value averaged over possible local orientations of the surface with respect to the ambient field (due to the surface roughness) is $G_{2s} \approx 1.4\times10^{-13}$ cm^2/s in $B = 4.6$ T and essentially temperature-independent. This yields the slope $d\sigma_{as}/d\sigma_{bs} \sim 3\times10^{-3}$. Then we find from Eq. (3) the corresponding $b \to c$ transition frequency shift

$$\frac{d\Delta\nu_{bc}}{d\sigma_{bs}} = \frac{\hbar}{ml}(a_s - a_t)\frac{G_{2s}}{K_{abs}} \sim -1.2\times10^{-7}\text{Hz}\cdot\text{cm}^2 \tag{6}$$

This is an order of magnitude less than the experimentally observed slope of $\Delta\nu_{ab}(\sigma_{bs})$. Note, that the extrapolation of the 3D experimental data [7] to the 2D case within the scaling approach $n_a \to \sigma_a/l$ gives essentially the same value as Eq.(6).

It is also remarkable that the part of σ_{as} independent of σ_{bs} (see Eq. (5)) contributes to the apparent wall shift $\Delta A_w(0)$ given by the extrapolation of the experimental $\Delta\nu_{ab}(\sigma_{bs})$ to zero density. Assuming $G_{1s} \sim G_1$ this contribution may be estimated as

$$\frac{\delta A_w}{h} \simeq \left(\frac{\gamma_p}{\gamma_e}\right)\frac{2\hbar}{ml}(a_s - a_t)\frac{G_{1s}}{K_{abs}} \sim -420\,\text{Hz}. \tag{7}$$

We should emphasize that, in contrast to the $b \to c$ transition, the $b \to a$ resonance is unaffected by the presence of residual a atoms, as follows from the general statement of Zwierlein *et al.* [3].

So far, we assumed the wall shift ΔA_w in Eq. (1) to be density independent. However, there are indications that this may not be true. In particular, Morrow *et*

al. [14] and Jochemsen *et al.* [15] measured the wall shift in zero field on the surface of ^{4}He and ^{3}He and found $\Delta A_w(^4\mathrm{He}) = -49(2)$ kHz and $\Delta A_w(^3\mathrm{He}) = -23(2)$ kHz. This was attributed to a wider surface profile of ^{3}He as compared to ^{4}He, which results in a wider and more shallow minimum of the adsorption potential for H atoms. Consequently, the wavefunction of adsorbed atoms spans farther from the surface, the average distance between hydrogen and helium atoms is increased and the electric polarization of hydrogen, which is responsible for the wall shift, is reduced.

Remarkably, the behavior of ΔA_w very closely resembles that of the binding energy E_a of hydrogen to the helium surface, namely, $E_a = 1.14$ [11, 14] and 0.40 K [15] for ^{4}He and ^{3}He, respectively. Moreover, the binding energy of hydrogen linearly decreases with an increase in the occupation of the surface state of ^{3}He [11]. A respective 6% decrease in ΔA_w was observed by Ahokas *et al.* [4] upon the addition of ^{3}He such that E_a should decrease by $\sim 10\%$. The above similarity has a deep grounding: according to the second-order perturbation theory, a fractional change in the unpaired electron density at the proton is $\Delta|\psi_e(0)|^2/|\psi_e(0)|^2 \simeq -2V/E_{\mathrm{H}}$, where E_{H} is the average energy for the excited states of H and V is the interaction energy [16], which is seemingly the binding energy E_a in our case. Thus, we may intuitively write

$$\frac{\delta(\Delta A_w)}{\Delta A_w} \sim \frac{\delta E_a}{E_a}. \tag{8}$$

Interaction of adsorbed H atoms with each other also changes E_a. In a thermal cloud of b atoms ($g^{(2)} = 2$),

$$\delta E_a = E_{\mathrm{int}} = -2\sigma_b \tilde{U}_t, \tag{9}$$

where $\tilde{U}_t \simeq 4\pi\hbar^2 a_t/ml \simeq 5\times10^{-15}$ K cm^2 is the effective vertex of the triplet interaction in 2D [17]. Combining Eqs. (8) and (9) we finally obtain the estimate

$$\frac{\delta(\Delta A_w)}{\Delta A_w} \sim -\frac{2\sigma_b\tilde{U}_t}{E_a} \simeq -10^{-14}\mathrm{cm}^2 \times \sigma_b. \tag{10}$$

For the apparent $b \to a$ frequency shift this gives

$$\Delta\nu_{ab} \sim 2.3\times10^{-10}\mathrm{Hz}\cdot\mathrm{cm}^2 \times \sigma_b, \tag{11}$$

about six times less than the experimental value of C_1.

To our knowledge, this is the first mentioning of the density-dependent wall shift of the hyperfine constant. This shift is associated with pair interaction. Therefore, like the contact shift in alkalies [2], it must decrease by a factor of two when the 2D hydrogen undergoes the 2D analogue of Bose-Einstein condensation, i.e., becomes locally coherent [18].

Strictly speaking, the H-H collisions may also contribute to a *negative* shift of A, by the analogy with the hyperfine pressure shift of H atoms in a helium atmosphere [19]. Unfortunately, the experimental data on the H-H pressure shift are unavailable. Theoretical calculation of the effect is a formidable problem even in free space, let alone the present 2D case (see, e.g., similar calculations for hydrogen in a helium buffer gas [20]).

Combining Eqs. (1), (6) and (11) we finally obtain that the effect of residual a atoms on ν_{bc} and the density-dependent wall shift of ν_{ab} together amount to about 30% of the frequency shift observed in experiment [4]. We regard this as a qualitative agreement in view of a rather large uncertainty in the value of the two-body relaxation rate constant G_2, the approximate character of Eq. (8) and the absence of experimental data on the effective vertex $\tilde{U}$. In addition, the H-H interaction in the adsorbed phase may differ from the one characterized by the quoted value of $\tilde{U}$ owing to substrate-mediated effects [6]. Obviously, the measurement of the surface density of a atoms would provide a direct check of the two contributions to the apparent hyperfine frequency shift, as discussed in this work.

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